

A MULTI-COMPONENT CATALYST SYSTEM FOR  
THE POLYCONDENSATION MANUFACTURE OF POLYESTERS

[0001] This application is a continuation-in-part of application Serial No.

5 10/303,977, filed November 26, 2002, incorporated by reference herein.

TECHNICAL FIELD

[0002] This invention relates to new multi-component catalyst systems for the  
10 polycondensation of polyesters. In a particular aspect, this invention pertains to  
novel multi-component germanium based catalyst systems for the polycondensation  
of PET (polyethylene terephthalate) used in the manufacture of bottles, fibre and  
film.

15 BACKGROUND OF THE INVENTION

[0003] It is well known in the polycondensation catalyst field that there are three  
primary polycondensation catalysts, based on the metals titanium, antimony and  
germanium. Titanium (Ti) displays the highest activity but it has the disadvantage  
20 that it generates a large range of undesirable side reactions which produce a polymer  
with a problematic yellow discoloration. For instance, in the case of polyethylene  
terephthalate polymers, once the polymer is formed, it is very difficult to colour  
correct.

25 [0004] An antimony (Sb) based catalyst, such as antimony trioxide, is the most  
commercially used type of catalyst. However, it too requires color correction. This  
is believed to be due to the fact that particulate antimony remains in the polymer  
thereby resulting in a grey discoloration in the polymer. There is a growing health  
concern issue that relates to the use of antimony in manufacturing polymers that will  
30 contact food. Such food may thereby absorb antimony. Additionally there are  
significant environmental concerns regarding the disposal of an antimony-containing  
distillate which is an inevitable by-product of the polycondensation reaction.  
Finally, there are considerable environmental issues relating to up-stream processing  
of antimony catalysts.

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[0005] Germanium (Ge), from a chemical and polymer discoloration viewpoint, has  
no negative implications as a polycondensation catalyst. However, germanium is  
costly and its cost is prohibitive to all but the highest quality polymer producers.  
Significant research has been invested in the discovery of catalyst formulations

which combine the benefits of the three catalyst elements described above whilst at the same time eliminating undesirable characteristics. In the case of germanium, this essentially has led to the incorporation of additional active elements or compounds which maintain catalytic reactivity but reduce cost without adversely affecting the polymer quality. In much of the prior art, germanium has traditionally been used as a component to increase the quality of polymer produced by catalysts such as titanium or antimony.

[0006] Prior literature discloses many ways of adding germanium to a polycondensation reaction. For example Japanese patent JP 2001019753A2 published January 23, 2001, assigned to Meldform Metals, details the complexing of germanium dioxide with a range of carboxylic acids, to produce an aqueous solution containing germanium dioxide in a concentration of 10 to 20 wt. %.

[0007] Other patents have disclosed the use of synergistic catalyst enhancers, containing carboxylic acids, in combination with titanium-containing catalysts. For instance, U.S. Patent No. 6,372,879 B1, granted April 16, 2002, assigned to ATOFINA Chemicals Inc., describes a range of synergistic combinations with a titanium-containing catalyst and lithium, sodium, potassium, rubidium, cesium, beryllium, magnesium, calcium, strontium, barium and ammonium salts.

[0008] U.S. Patent No. 6,258,925 B1, granted July 10, 2001, assigned to ATOFINA, discloses a titanyl oxalate catalyst and a catalyst enhancer such as a metallic oxalate, for example, lithium oxalate.

[0009] WO 00/71252 A1, published November 30, 2000, assigned to ACMA Limited, discloses a catalyst composition for use in the preparation of esters, comprising an organometallic compound which is a reaction product of an orthoester or condensed orthoester of titanium, zirconium or aluminium, used in combination with a compound of germanium, antimony or tin. In this case, the preferred orthoester has the formula  $M(OR)_4$  or  $Al(OR)_3$  where M is titanium or zirconium and R is an alkyl group, and the condensed orthoester typically being of the formula  $R_1O[M(OR_1)_2O]_nR_1$ . These organometallic compounds are prepared by reacting the orthoester and the metallic compound in the presence of, preferably, a dihydric alcohol such as 1,2-ethanediol.

**[0010]** U.S. Patent No. 6,365,659 B1, granted April 2, 2002, assigned to Toray Industries Inc., discloses a polyester composition comprising a polyester and a compound oxide of titanium as an essential element and a metal element selected from the group consisting of aluminium, zirconium germanium, tin and silicon.

5 Specific particle size distribution for these catalysts in the polyester is stated.

**[0011]** WO 0156694 A1, published August 9, 2001, assigned to ACMA Limited, discloses the combination of an organometallic compound containing either titanium or zirconium with a second metal from the group consisting of germanium, tin and  
10 antimony and a carboxylic acid. In the preferred embodiment a hydroxy alcohol and a base are also present.

**[0012]** WO 9322367 A1 / EP0591488A1, assigned to Rhone Poulenc Viscosuisse SA, refers to a dual polycondensation catalyst system comprising lithium and  
15 germanium. The invention concerns a method of producing, without using antimony, a polyester from poly(ethylene terephthalate) units. Following esterification, a mixed catalyst consisting of 10 to 75 parts per million of lithium and 15 to 80 parts per million of germanium is used for polycondensation. The antimony-free polyester thus obtained is purportedly suitable for use in the manufacture of bottles,  
20 sheeting, film, fibre, filaments and molded articles.

**[0013]** U.S. Patent No. 5,417,908, assigned to Rhone Poulenc Viscosuisse SA, granted May 23, 1995, describes a polyester manufactured using manganese as an esterification catalyst, de-activating the manganese with phosphoric acid and  
25 subsequently adding germanium as the primary polycondensation to form a polyethylene terephthalate polyester.

**[0014]** WO 99/28033, assigned to Tioxide Specialities Limited, discloses the use of an organometallic catalyst which is a reaction product of an orthoester or condensed  
30 orthoester of titanium, zirconium or aluminium, an alcohol with at least two hydroxyl groups, an organophosphorous compound and a base.

**[0015]** U.S. Patent No. 6,358,578 B1, assigned to Zimmer AG, granted March 19, 2002, describes a product which uses high surface area activated charcoal to  
35 promote the activity of a polycondensation catalyst such as antimony, titanium, lead, germanium, zinc and tin.

[0016] U.S. patent application No. 2003/0045673 A1, published March 6, 2003, Nakajima et al., filed December 25, 2000, discloses a polyester polymerization catalyst comprising at least one kind selected from the group consisting of aluminum and compounds thereof as a first metal-containing component, characterized in that the thermal stability parameter (TS) of polyethylene terephthalate (PET) polymerized by the polyester polymerization catalyst satisfies the following formula (1):

$$TS < 0.30 \quad (1)$$

wherein TS is a numerical value calculated in the formula;

$$TS = 0.245 \{ [IV]_f^{-1.47} - [IV]_i^{-1.47} \}$$

from the final intrinsic viscosity ( $[IV]_f$ ) which is determined after 1 g Pet having an initial intrinsic viscosity ( $[IV]_i$ ) of approximately 0.65 dl/g is placed in a glass test tube, vacuum-dried at 130°C for 12 hours, and maintained in a molten state at 300°C for 2 hours in a non-circulating nitrogen atmosphere

## SUMMARY OF THE INVENTION

[0017] The catalyst systems according to the invention are new types of polycondensation catalysts and have particular application to the polycondensation reaction of the monomer bis-hydroxy-ethyl terephthalate (BHET) at elevated temperature and reduced pressure to produce high quality polyethylene terephthalate (PET). The catalyst systems described herein are comprised of a core germanium catalyst and one or more specified enhancers.

[0018] A multi-component catalyst system for the polycondensation of a polyester monomer comprising the element germanium and one or more catalyst enhancers selected from the group of elements consisting of one or more of aluminium, silicon, molybdenum, manganese, lithium and combinations thereof, excepting the combination of germanium and lithium only, said elements being in the form of polycondensation compatible acids, bases, compounds, salts, compositions, oxides or organic complexes. The monomer may be bis-hydroxy-ethyl terephthalate, which can be polycondensed to produce polyethylene terephthalate.

[0019] When the catalyst system comprises germanium and aluminium, the level of germanium in the polyethylene terephthalate can be in the range from 1 part per million to 200 parts per million and the level of aluminium in the polyethylene terephthalate can be in the range from 1 part per million to 400 parts per million. More specifically, the level of germanium can be 5 to 100 parts per million and the

level of aluminium can be 20 to 200 parts per million. Preferably, the level of germanium can be 5 to 60 parts per million and the level of aluminium can be 60 to 150 parts per million.

5    **[0020]** When the catalyst system comprises germanium and silicon, the level of germanium in the polyethylene terephthalate can be in the range from 1 part per million to 200 parts per million and the level of silicon in the polyethylene terephthalate can be in the range from 1 part per million to 400 parts per million. More specifically, the level of germanium can be 10 to 80 parts per million and the  
10   level of silicon can be 10 to 200 parts per million. Preferably, the level of germanium can be 20 to 60 parts per million and the level of silicon can be 20 to 150 parts per million.

15   **[0021]** When the catalyst system is germanium and molybdenum, the level of germanium in the polyethylene terephthalate can be 1 to 200 parts per million and the level of molybdenum in the polyethylene terephthalate can be 1 to 200 parts per million. More specifically, the level of germanium can be 1 to 100 parts per million and the level of molybdenum can be 1 to 100 parts per million. Preferably, the level of germanium can be 5 to 60 parts per million and the level of molybdenum  
20   can be 1 to 60 parts per million.

25   **[0022]** When the catalyst system comprises germanium and manganese, the level of germanium in the polyethylene terephthalate can be 1 to 200 parts per million and the level of manganese in the polyethylene terephthalate can be 1 to 400 parts per million. More specifically, the level of germanium can be 10 to 80 parts per million and the level of manganese can be 10 to 200 parts per million. Preferably, the level of germanium can be 20 to 60 parts per million and the level of manganese can be 20 to 150 parts per million.

30   **[0023]** When the catalyst system is germanium and lithium, and one or more of aluminium, silicon, molybdenum and manganese, the level of germanium in the polyethylene terephthalate can be 1 to 200 parts per million and the level of lithium in the polyethylene terephthalate can be 1 to 200 parts per million. More specifically, the level of germanium can be 5 to 60 parts per million and the level of  
35   lithium can be 10 to 80 parts per million. Preferably, the level of germanium can be 5 to 30 parts per million and the level of lithium can be 20 to 70 parts per million.

5 [0024] When the catalyst systems comprise germanium, aluminium and silicon, or germanium, aluminium and molybdenum, or germanium, aluminium and manganese, or germanium, aluminium and lithium, or germanium, silicon and molybdenum, or germanium, silicon and manganese, or germanium, silicon and lithium, or  
10 germanium, molybdenum and manganese, or germanium, molybdenum, and lithium, or germanium, manganese and lithium, the level of germanium in the polyethylene terephthalate can be in the range from 1 part per million to 200 parts per million, the level of aluminium in the polyethylene terephthalate can be in the range from 1 part per million to 200 parts per million, the level of silicon can be 1  
15 part per million to 200 parts per million, the level of molybdenum can be 1 part per million to 200 parts per million, the level of manganese can be 1 part per million to 200 parts per million, and the level of lithium can be 1 part per million to 200 parts per million.

15 [0025] The catalyst system can also comprise germanium, aluminium, silicon and molybdenum, or germanium, aluminium, silicon and manganese, or germanium, aluminium, silicon and lithium or germanium, silicon, molybdenum and manganese, or germanium, silicon, molybdenum and lithium, or germanium, molybdenum, manganese and lithium, or germanium, aluminium, molybdenum and manganese, or  
20 germanium, aluminium, manganese and lithium, or germanium, silicon, molybdenum and manganese, or germanium, aluminium, molybdenum and lithium, or germanium, silicon, manganese and lithium, or germanium, aluminium, silicon, manganese and molybdenum, or germanium, aluminium, silicon, manganese and lithium, or germanium, silicon, manganese, molybdenum and lithium, or germanium, aluminium, silicon, molybdenum and lithium, the level of germanium in the polyethylene terephthalate can be in the range from 1 part per million to 200 parts per million, the level of aluminium can be in the range from 1 part per million to 200 parts per million, the level of silicon in the polyethylene terephthalate can be in the range from 1 part per million to 200 parts per million, the level of molybdenum  
25 in the polyethylene terephthalate can be in the range from 1 part per million to 200 parts per million and the level of manganese in the polyethylene terephthalate can be in the range from 1 part per million to 200 parts per million, and the level of lithium in the in the polyethylene terephthalate can be in the range from 1 part per million to 200 parts per million.

35 [0026] The invention is also directed to a multi-component catalyst system for the polycondensation of a polyester monomer comprising the element germanium and

the catalyst enhancers aluminium and lithium, said elements being in the form of polycondensation compatible elements, compounds, acids, bases, salts, compositions, oxides or organic complexes. The monomer can be bis-hydroxy-ethyl terephthalate, which can be polycondensed to produce polyethylene terephthalate.

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[0027] The level of germanium in the polyethylene terephthalate can be in the range from 1 part per million to 200 parts per million, the level of aluminium in the polyethylene terephthalate can be in the range from 1 part per million to 200 parts per million and the level of lithium in the polyethylene terephthalate can be in the range from 1 part per million to 200 parts per million.

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[0028] More specifically, the level of germanium can be 5 to 100 parts per million, the level of aluminium can be 20 to 200 parts per million and the level of lithium can be 10 to 80 parts per million.

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[0029] Even more specifically, the level of germanium can be 5 to 30 parts per million, the level of aluminium can be 60 to 150 parts per million and the level of lithium can be 20 to 70 parts per million.

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[0030] Without attempting to provide an exhaustive list, the aluminium can be incorporated in the catalyst system as a phenoxide, a lactate, a stearate, a glycolate, an oxalate, a citrate or a tartrate. Without attempting to provide an exhaustive list, the lithium can be incorporated in the catalyst system as a hydroxide, an acetate, a citrate, a carbonate or an oxalate.

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#### DETAILED DESCRIPTION OF THE INVENTION

[0031] Throughout the following description, specific details are set forth in order to provide a more thorough understanding of the invention. However, the invention may be practiced without these particulars. In other instances, well known elements have not been shown or described in detail to avoid unnecessarily obscuring the invention. Accordingly, the specification and drawings are to be regarded in an illustrative, rather than a restrictive, sense.

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[0032] We have discovered that a range of specific elements, which independently show limited catalytic activity, can significantly enhance the activity of germanium as a polycondensation catalyst. For the purposes of this disclosure, we have

described these elements as “enhancers”. It is understood that the term “enhancer” includes any element or substance which improves the performance of a polyester condensation catalyst notwithstanding that the element or substance per se may have limited catalytic activity. A synergistic relationship has been discovered between  
5 these catalyst enhancers and germanium-based catalysts. We have found that aluminium, silicon, molybdenum or manganese used either independently with germanium or in a mixed combination (which can include lithium) exhibits a high catalyst activity when compared to a PET polycondensation product catalysed by germanium only, or the activity of the enhancer only, or the sum of their independ-  
10 ent activities. This synergistic effect enables a polycondensation polymer of high quality to be produced without entailing the costs normally associated with a germanium only-catalysed polymer.

**[0033]** It should be understood that in the discussion herein, and in the claims, when  
15 we refer to the elements germanium, aluminium, silicon, molybdenum, manganese and lithium, we are referring to the use of those elements in any conceivable polycondensation catalyst system, including but not limited to the acids, bases and salts of these elements, compositions containing these elements, compounds incor-  
20 porating these elements, oxides or organic complexes of germanium and the catalyst enhancers aluminium, silicon, molybdenum, manganese and lithium. It is under-  
stood that in referring to the foregoing elements and substances, we are contemplat-  
ing only those elements and substances that are compatible with polyester  
polycondensation systems in the quantities and forms which catalyse the  
polycondensation of polyester.

25  
**[0034]** The use of our catalyst enhancers in appropriate amounts and forms reduces the germanium requirement and thereby reduces catalyst cost thereby enabling the benefits of germanium-catalysed PET to be gained in markets which otherwise  
30 would be excluded on a cost basis. We have found that it is possible according to the invention to maintain optimum catalyst quality. It is also possible after adjust-  
ment of the ratios of the respective elements to produce an antimony-free alternative catalyst system at a competitive cost.

**[0035]** Examples of catalyst combinations that demonstrate the subject invention are  
35 given in Table 1. However, it should be understood that those examples do not represent the full range of catalyst levels which have displayed the synergistic effect and accordingly the scope of the invention is not limited thereby. It should also be



understood that the combinations which demonstrate the highest levels of catalytic activity do not necessarily produce PET with the most preferred characteristics. For the purposes of these tests germanium content in the polyester has been most preferably used in the range from 5 to 60 parts per million. However, beneficial effects have been observed in the range from 1 to 200 parts per million germanium.

[0036] For aluminium in combination with a germanium catalyst, synergy has been observed in the range from 1 to 400 parts per million. However, the preferable range of aluminium is 20 to 200 parts per million and ideally 60 to 150 parts per million, dependant upon the levels of the catalyst employed.

[0037] For silicon in combination with a germanium catalyst, synergy has been observed in the range from 1 to 400 parts per million. However, the preferable range of silicon is 20 to 200 parts per million and ideally 60 to 150 parts per million, dependant upon the levels of the catalyst employed.

[0038] Molybdenum has been investigated in combination with germanium in the range from 1 to 200 parts per million levels with significant catalytic activity being observed at low levels, specifically with the level of molybdenum being in the range or 1 to 100 parts per million and the most preferred range being 1 to 60 parts per million molybdenum.

[0039] Manganese has displayed germanium enhancer properties in the range from 1 to 400 parts per million, more specifically 10 to 200 parts per million, and the most preferred being in the range from 20 to 60 parts per million.

[0040] Lithium in combination with one or more of aluminium, silicon, molybdenum and manganese has demonstrated germanium enhancer activity in the range from 1 to 200 parts per million, the most preferred levels being 10 to 80 parts per million and ideally 20 to 70 parts per million.

[0041] It should be understood that these optimized catalyst loadings are dependent upon the germanium level, and, particularly with respect to catalyst systems including two or more enhancers, the other components within the system.

[0042] A primary advantage of the germanium enhancers we have discovered is that it is possible to obtain high quality polymer manufactured using reduced germanium

levels. Therefore, a significant benefit of our catalyst system according to the invention is reduced cost and the opportunity for replacement of heavy metal catalysts in lower value applications. Without being adversely bound by any theories, but in the interests of explaining the invention, we believe that novelty in the invention resides in the synergistic effects on the catalytic activity that we have observed when combining the previously mentioned catalyst enhancers with germanium. We have described the elements as catalyst enhancers rather than catalysts due to their relatively limited activity when used independently, compared with the remarkable activity that we have discovered when they are used in combination with germanium. The enhancer elements we have discovered have not to our knowledge been demonstrated within the prior art and have negligible independent catalytic activity, but surprisingly display significant levels of activity when combined with germanium.

[0043] Advantages of the catalyst systems we have discovered are fast reaction rate, lower cost, lower catalyst (metal) addition, and comparable polymer quality to commercial PET products using commercially available catalysts.

#### EXAMPLE 1

[0044] Catalyst testing was carried using a conical 5-L stainless steel oil-jacketed reaction vessel. The experiments were carried out at a controlled melt temperature of 280°C and at pressures of typically less than 1 mbar. The reaction melt was agitated by a vertically mounted helical stirrer operating at a constant speed (100 rpm). The stirrer motor's amperage was monitored. The reaction is considered to be complete when an amperage generating a torque equivalent to an intrinsic viscosity of 0.6 is attained. (Intrinsic Viscosity (IV), is an indication of polymer chain length and thus degree of polymerisation.) Distillates generated by both the pre-polycondensation and the polycondensation steps were collected separately.

Catalyst-free BHET (bis-hydroxy-ethyl terephthalate) was typically used eliminating the need for the suppression of esterification catalysts. Catalysts and stabilisers were added to the vessel at the time of BHET charging and air was removed from the system prior to the reaction commencing. Information relating to the oil and reaction temperatures, the pressure within the vessel, the stirrer speed and torque was automatically logged every 10 seconds to enable accurate batch to batch correlation to be attained. For comparison calibration purposes, test batches containing commercially available germanium-containing catalysts were periodically

completed. These experiments provided a catalyst activity template against which different catalyst systems could be easily compared. Typical reaction times for germanium-catalysed polycondensation over a range of catalyst loadings are described in Table 1 below. Table 1 below also tabulates results obtained from  
5 conducting polycondensation tests using various metals, alone or in combination.

TABLE 1

	Test Number for Patent	Catalyst Type	Catalyst Loading ppm	Polyc n Time mins	IV LSP
5	Ge Template 3				
	A1	Ge Only	100	84.9	0.607
	A2	Ge Only	100	85.1	0.612
	A3	Ge Only	80	93.6	0.608
	A4	Ge Only	80	92.0	0.635
10	A5	Ge Only	60	105.5	0.608
	A6	Ge Only	60	104.3	0.624
15	A7	Sb Only	200	108.2	0.603
	A8	Li Only	200	Abandoned	
	A9	Li Only	80	Abandoned	
20					
	A10	Al Only	120	Abandoned	
	A11	Ge/Al	60/60	68.5	0.613
	A12	Ge/Al	60/30	83.5	0.616
	A13	Ge/Al	60/25	96.5	0.603
	A14	Ge/Al	50/43	90.0	0.618
	A15	Ge/Al	45/45	103.0	0.623
	A16	Ge/Al	40/53	83.5	0.624
25	A17	Ge/Al	30/60	88.5	0.615
	A18	Ge/Al	20/80	93.6	0.600
	A19	Ge/Al	10/200	133.7	0.586
	A20	Ge/Al	60/150	59.0	0.608
30					
	A21	Mo Only	200	111.6	0.578
	A22	Mo Only	60	118.1	0.575
	A23	Ge/Mo	60/60	26.7	0.560
	A24	Ge/Mo	60/20	30.8	0.574
	A25	Ge/Mo	60/5	35.8	0.581
	A26	Ge/Mo	30/5	54.3	0.578
	A27	Ge/Mo	30/5	55.3	0.573
35	A28	Ge/Mo	5/60	63.3	0.560
	A29	Ge/Al/Si	45/45/15	87.5	0.611
	A30	Ge/Al/Li	45/45/45	83.6	0.605
40					
	Ge Template 2				
45	B1	Ge Only	80	100.5	0.594
	B2	Ge Only	60	115.7	0.610
	B3	Ge Only	60	116.7	0.602
	B4	Ge Only	40	132.0	0.618
50	B5	Si Only	200	Abandoned	
	B6	Ge/Si	60/155	83.5	0.591
	B7	Ge/Si	60/20	99.5	0.580
	B8	Ge/Si	40/103	107.2	0.592
	B9	Ge/Si	40/34	123.0	0.608
	B10	Mn Only	200	136.0	0.598
55	B11	Ge/Mn	50/21	117.0	0.606

A10: Al only; 120 ppm Al as tartrate

A9: Li only; 80 ppm as oxalate

The term "abandoned" in tests A8, A9, A10 and B5 means that the tests were stopped after there was no increase in torque after two hours at the standard polycondensation temperature and pressure.

### Test Criteria and Results of Testing

[0045] All BHET used was free from esterification catalysts in order to eliminate any potential interaction with the polycondensation catalysts tested.

- 5 [0046] Phosphorus was added as a thermal stabiliser and in some processes it was also added to deactivate esterification catalysts prior to beginning polycondensation. It is known that phosphorus can affect the activity of polycondensation catalysts and therefore all tests were performed with a reasonable level (40 parts per million) of phosphorus added as  $H_3PO_4$ .

10

[0047] Control samples containing germanium only were tested to produce a template. All new catalysts were tested against a germanium-only template of 40 to 100 parts per million addition. Care was taken to produce a new template following any maintenance work on the PET reactor that might affect the process control  
15 characteristics. The examples described show tests performed versus two templates (A and B) which were produced following a change of temperature control equipment.

- [0048] Referring to Table 1, samples A1 - A6 were tested at 60, 80 and 100 parts  
20 per million germanium addition. The reproducibility of tests was shown to be very good. Also, a standard commercially available antimony catalyst (A7) was tested in order to compare activity and total catalyst loading. Aluminium, lithium and molybdenum were tested against this template. Each element was tested on its own and in combination with germanium at various levels.

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[0049] Samples B1 - B4 were tested at 40, 60 and 80 parts per million germanium addition. The reproducibility of tests was shown to be very good. Silicon and manganese were tested against this template. Each element was tested on its own and in combination with germanium at various levels.

30

[0050] During any test campaign, germanium-only tests were performed at regular intervals to ensure no drift from the template.

### Lithium - Samples A8 - A9

- 35 [0051] Lithium showed no catalytic activity on its own even at 200 parts per million addition. When combined with germanium, however, the germanium activity was enhanced. It appears that the enhanced activity is limited, with approximately the

same activity achieved with the lithium addition varied between 10 and 80 parts per million.

Aluminium - Samples A10 - A20

5 [0052] Aluminium showed limited catalytic activity on its own. However, when combined with germanium, aluminium enhanced the catalytic activity of the germanium. Various germanium/aluminium levels are shown, each of which shows significantly enhanced activity compared with the same level of germanium on its own. In fact, even at 20 parts per million germanium addition (A18), an equivalent  
10 activity to germanium only at 80 parts per million addition is achieved. At this level, the activity is greater than a standard antimony catalyst addition of 200 parts per million (A7), and the catalyst contains only 50% of the metallic addition levels as the antimony catalyst, and is much less expensive than the equivalent germanium-only catalyst.

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Molybdenum - Samples A21 - A28

[0053] Molybdenum showed some catalytic activity on its own. However, when combined with germanium, molybdenum enhanced the catalytic activity of the germanium by a much greater amount than would be expected based on the molybdenum activity on its own. Various germanium/molybdenum levels are shown, each  
20 of which shows significantly enhanced activity compared with the same level of germanium on its own. In fact, even at 5 parts per million germanium addition (A28), an equivalent activity to germanium only at more than 100 parts per million addition is achieved. At this level, the activity is much greater than a standard  
25 antimony catalyst addition of 200 parts per million, it contains only 32.5% of the metallic addition levels as the antimony catalyst, and it is much less expensive than the equivalent germanium-only catalyst.

Silicon - Samples B5 - B9

30 [0054] Silicon shows no significant catalytic activity on its own. However, when combined with germanium, silicon enhanced the catalytic activity of the germanium. Various germanium/silicon levels are shown, each of which shows enhanced activity compared with the same level of germanium on its own. At 40 parts per million germanium addition (B8, B9), an equivalent activity to germanium only of 50 to 60  
35 parts per million addition was achieved.

Manganese - Samples B10 - B11

5 [0055] Manganese showed some catalytic activity on its own. However, when combined with germanium, manganese enhanced the catalytic activity of the germanium by a greater amount than would be expected based on the manganese activity on its own. Various germanium/manganese levels have been tested, each of which demonstrated enhanced activity compared with the same level of germanium on its own. At 50 parts per million germanium addition (B11), an equivalent activity to germanium only of 60 parts per million addition was achieved.

#### Multi-Component Samples - A29-A30

10 [0056] The tests demonstrate that germanium content can be further reduced by combining the “enhanced” effect of two or more of the additives previously described. Tests A29 and A30 contain the same addition levels of germanium and aluminium as Test A15. However, the addition of a further promoting element, silicon in A29 and lithium in A30, enhanced the activity further from approximately  
15 60 parts per million germanium only equivalent to around 100 parts per million germanium only equivalent.

[0057] The information gained from the tests on the above-described reactor have been validated by external tests on both continuous and large-scale batch reactors.  
20 These tests have confirmed that, for the range of process and chemical operating parameters used, there is complete correlation with industrial equipment. The inventors are therefore confident that the invention is scientifically valid and is not due to any specific characteristic of the equipment used.

#### 25 EXAMPLE 2

[0058] Further tests have been performed and have provided the following data:

#### Ge/Al - Tests 203 - 210

30 [0059] The tests below demonstrate the effect on the activity of the catalyst system with variation in the ligand associated with the Al. These tests were conducted in the presence of a phosphoric acid stabilizer and a phosphorus level of 40 ppm was used.

35 [0060] From this data it is possible to conclude that with respect to activity alone the preferred ligands are lactate or glycolate. It should be noted that effects due to the ligand chemistry can be observed in other PET parameters including but not limited to color and optical clarity of the final polymer.

PET Rig Test No.	Catalyst Type	Catalyst Loading Ge/Al ppm	Polycon Time/Mins	IV LSP
202	Ge only	100/0	80.7	0.563
203	Ge/Al (Al as phenoxide)	30/100	79.1	0.531
204	Ge/Al (Al as isopropoxide)	30/100	138.6	0.631
205	Ge/Al (Al as lactate)	30/60	89.5	0.624
206	Ge/Al (Al as stearate)	30/100	115.6	0.596
207	Ge/Al (Al as glycolate)	30/100	81.3	0.596
208	Ge/Al (Al as oxalate)	30/100	92.1	0.603
210	Ge/Al (Al as citrate)	30/100	93.6	0.602

Ge/Al/Li - Tests 290 - 299

[0061] The following tests demonstrate a similar effect to that observed with Al, in this instance the ligand associated with the Li was varied and the chemistry of the germanium and the aluminium was kept constant.

[0062] Additionally, with the tests using lithium acetate the phosphoric addition was adjusted to determine the degree by which the activity would be effected.

PET Rig Test No.	Catalyst Type	Catalyst Loading Ge/Al/Li	Polycon Time/Mins	P ppm	IV LSP
290	Ge/Al/Li (Li as OH)	15/60/45	87.3	40	
296	Ge/Al/Li (Li as acetate)	15/60/45	71.8	40	
297	Ge/Al/Li (Li as acetate)	15/60/45	88.8	80	
298	Ge/Al/Li (Li as acetate)	15/60/45	88	80	
299	Ge/Al/Li (Li as citrate)	15/60/45	110.95	80	

[0063] It is reasonable to conclude from these tests that the preferred ligands associated with the lithium would be either the hydroxide or the acetate.



Ge/Al/Li - Effect of Phosphorus - Tests 274-278

PET Rig Test No.	Catalyst Type	Catalyst Loading Ge/Al/Li ppm	Total Time/Mins	P/ppm	IV LSP
5 274	Ge/Al/Li (Li as OH)	15/60/45	117.3	80	0.588
278	Ge/Al/Li (Li as OH)	15/60/45	98.8	0	0.591

[0064] From the above data (and in combination with that displayed in the foregoing tests involving Ge/Al and Ge/Al/Li) it is clear that a limited degree of catalyst  
 10 deactivation due to P is observed. It is believed that a level of P enhances the thermal stability of the polymer and the observed levels of deactivation are considered to be within acceptable limits.

Colour Information

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Sample	L*	a*	b*
T269 Ge only 100 ppm	69.88	-0.48	2.88
T274 Ge/Al/Li 15/60/45 ppm	69.16	-1.58	6.41
20 T278 Ge/Al/Li 15/60/45 EST (No Phosphoric)	70.81	-1.6	6.8
T302 Ge/Al/Li 15/60/45 EST (80ppm P) 10ppm Co	66.23	-1.1	1.3

[0065] The above color data is for polymer which has been produced by  
 25 esterification/polycondensation on the 1.5Kg laboratory reactor and has been analyzed using a HunterLab ColorQuest XE Spectrophotometer according to the CIE 1976 L\*a\*b\* scale where:

L\* is a measurement of lightness from 100 for perfect white to 0 for black;  
 b\* is a measurement of color which trends from red when positive to  
 30 grey at zero and green when negative; and  
 a\* is a measurement of color which trends from yellow when positive to grey at zero and blue when negative.

**[0066]** As will be apparent to those skilled in the art in the light of the foregoing disclosure, many alterations and modifications are possible in the practice of this invention without departing from the spirit or scope thereof. Accordingly, the scope of the invention is to be construed in accordance with the substance defined by the  
5 following claims.